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Measurement and Prediction of Water Outgassing from TR55 Silicone by the Isoconversional Technique

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Disclaimer

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Objective

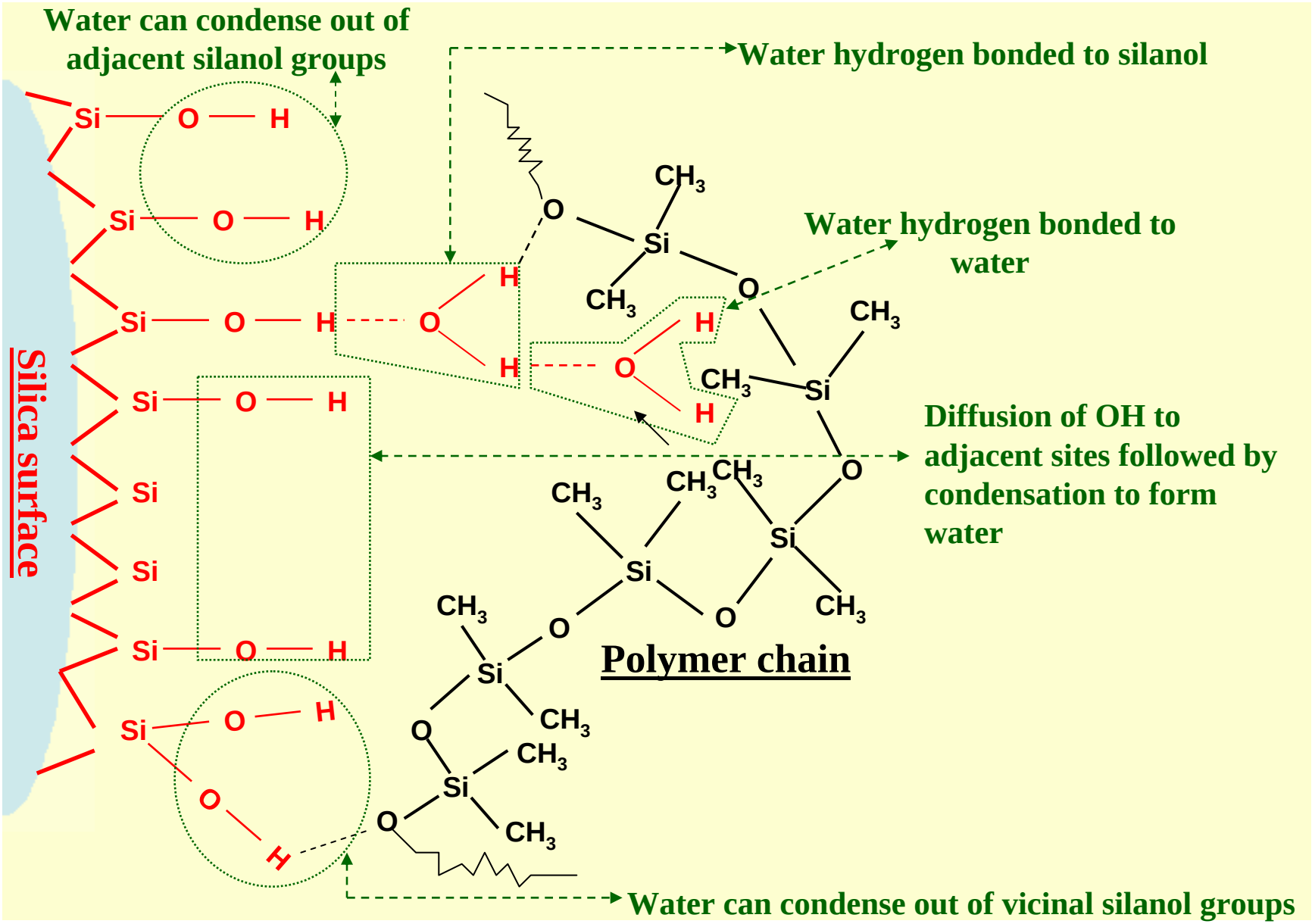
- To measure the H_2O outgassing kinetics of TR55 silicone after a few hours of vacuum pumping.
- To make H_2O outgassing kinetic predictions for TR55 at low temperatures in a vacuum/dry environment.

Composition of TR55

A Dow Corning commercial formulation:

70% polysiloxane gum and 30% fumed silica filler.

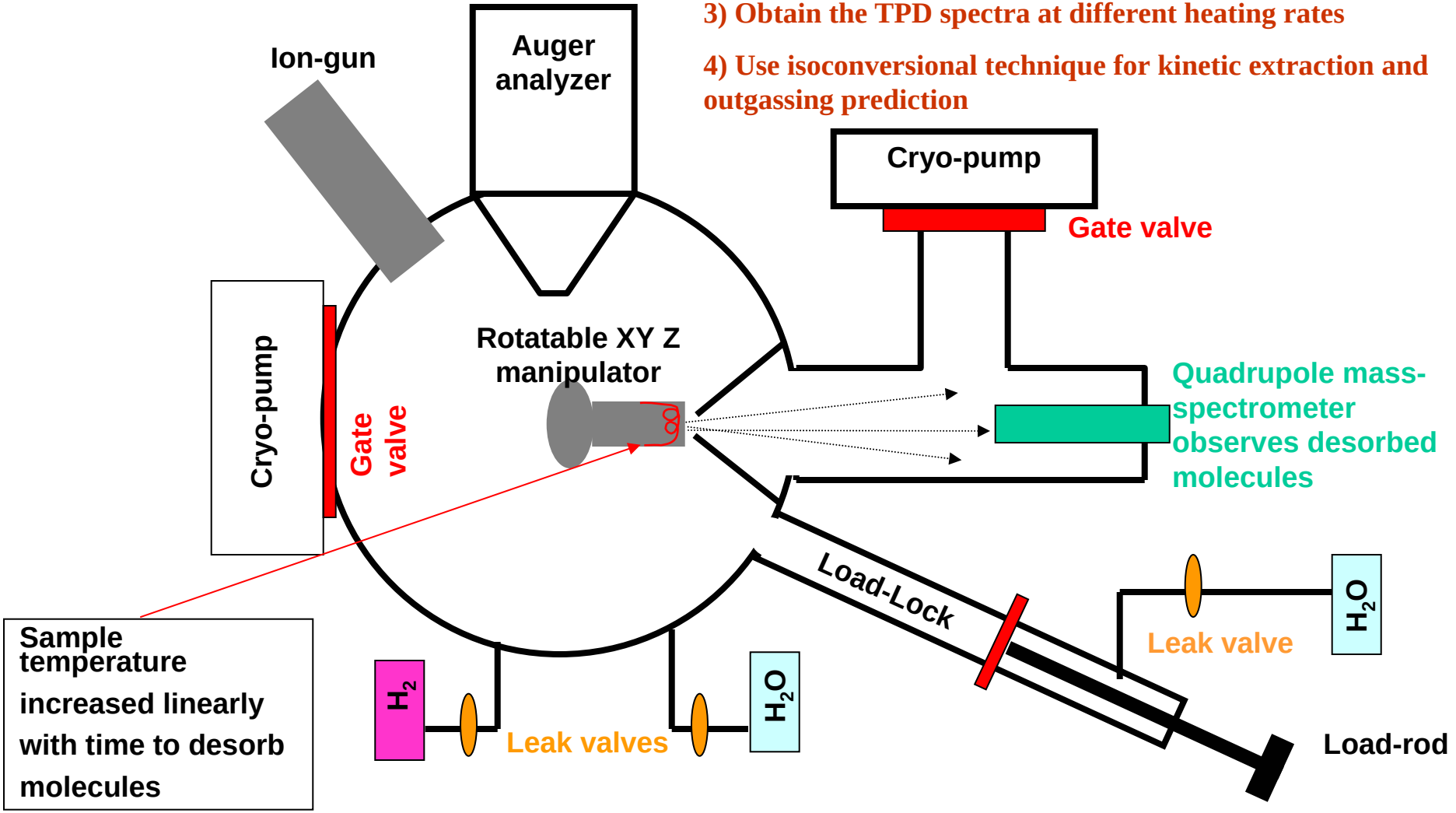
Silica filler surfaces have a high affinity for moisture and H_2O outgassing from silicone involve multiple energy barriers



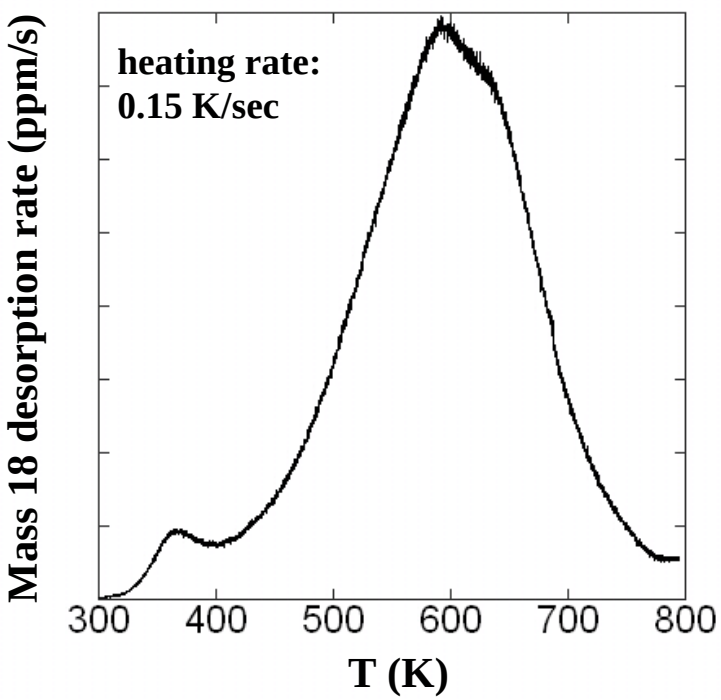
Our approach utilized linear heating technique to characterize the kinetics of the H_2O desorption

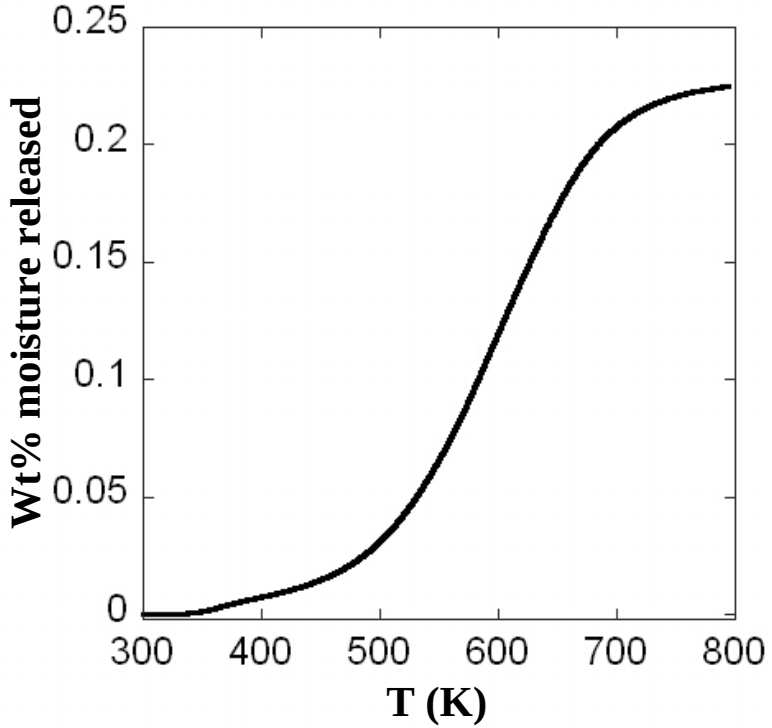
The steps:

1) Load sample onto the manipulator in the TPD chamber
2) Raise the sample's temperature linearly
3) Obtain the TPD spectra at different heating rates
4) Use isoconversional technique for kinetic extraction and outgassing prediction



There is approximately 0.23 wt% of potential moisture left in TR55 after a few hours of vacuum pumping





However, only a fraction of the moisture recorded by the broad TPD spectrum contributes to outgassing in a dry environment at lower temperatures

Isoconversional technique is currently employed for model-independent kinetics extraction and outgassing prediction

•Let α represent the fractional release of gas (or fraction reacted), then the heterogeneous solid-state reaction that releases gas is written as:[1]

•With β = dT/dt: $\frac{d\alpha}{dt} = k.f(\alpha) = \upsilon\, e^{-\frac{E}{RT}}.f(\alpha)$ or $\frac{d\alpha}{dT} = \left[\frac{\upsilon}{\beta}\cdot f(\alpha)\right]\cdot e^{-\frac{E}{RT}}$

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln\{\upsilon f(\alpha)\}$$ **[Friedman** method]

Both E and $\{\upsilon f(\alpha)\}$ can be obtained from the Friedman method[2].

The time prediction (t_α) of how long it takes for a specific conversion α to be reached at the isothermal temperature T_o can be obtained from the rate equation by integration:[3]

$$t_\alpha \equiv \int_0^{t_\alpha} dt = \int_0^{\alpha} \frac{d\alpha}{[\upsilon f(\alpha)]e^{-\frac{E}{RT_o}}}$$

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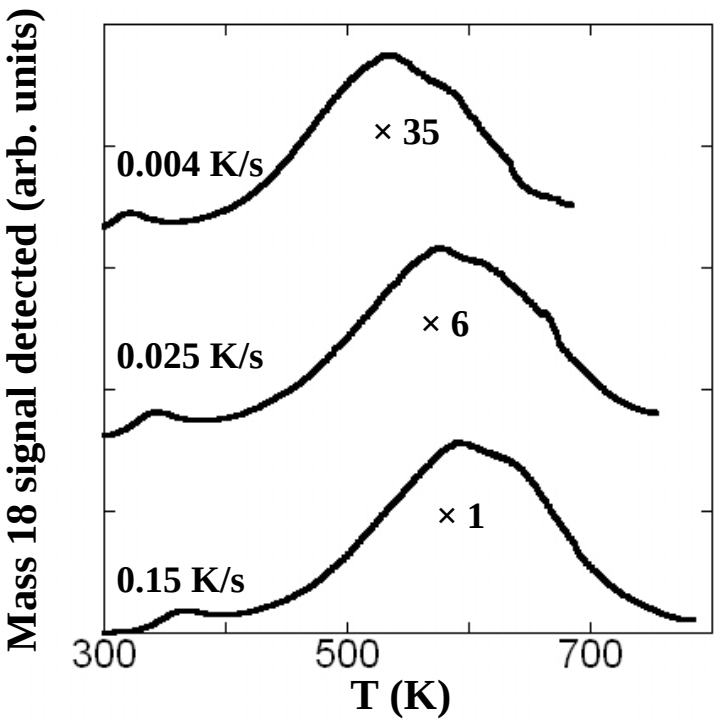
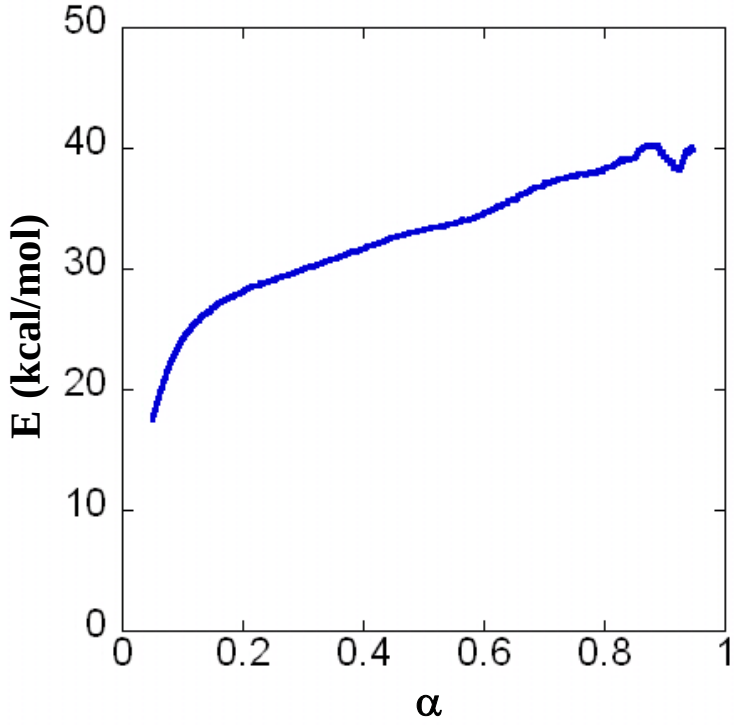
[1] **A. K. Galwey and M. E. Brown, *Thermal Decomposition of Ionic Solids*, Elsevier, New York, 1999.**

[2] **H. L. Friedman, J. Polym. Sci. 50, 183 (1965).**

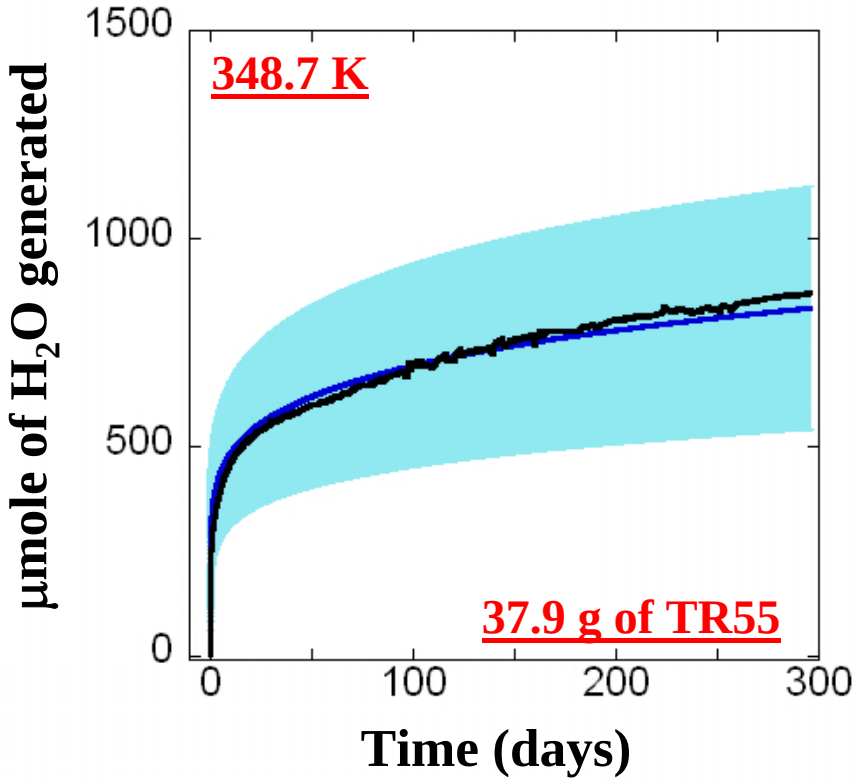
[3] **L. N. Dinh, A. K. Burnham, M. A. Schildbach, R. S. Maxwell, B. Balazs, W. McLean II, *Measurement and Prediction of H_2O Outgassing Kinetics from Silica-Filled Polydimethylsiloxane TR55 and S5370*,** submitted to Polymer Degradation and Stability.

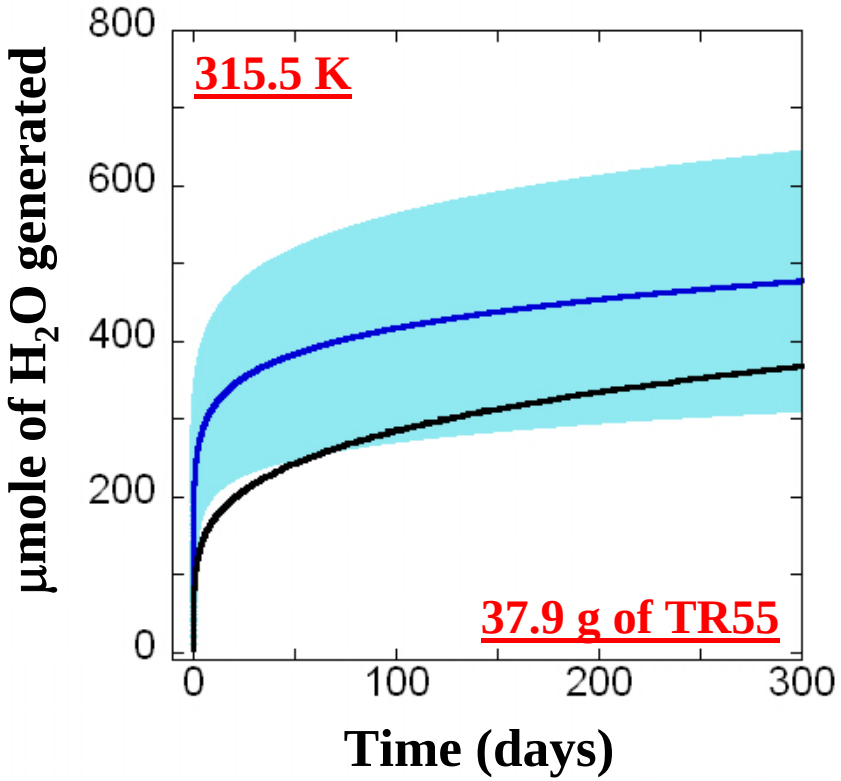




- **Isoconversional analysis indicates that the energy barrier for H_2O release from TR55 is an increasing function of the fractional H_2O release.**
- **This can be interpreted as the release of H_2O from physisorbed water, then chemisorbed water with decreasing OH density from the surfaces of embedded silica particles. At $\alpha > 0.5$, some of the moisture released may be due to the decomposition of TR55.**

Comparisons between isoconversional kinetic predictions and isothermal long-term H_2O outgassing from TR55





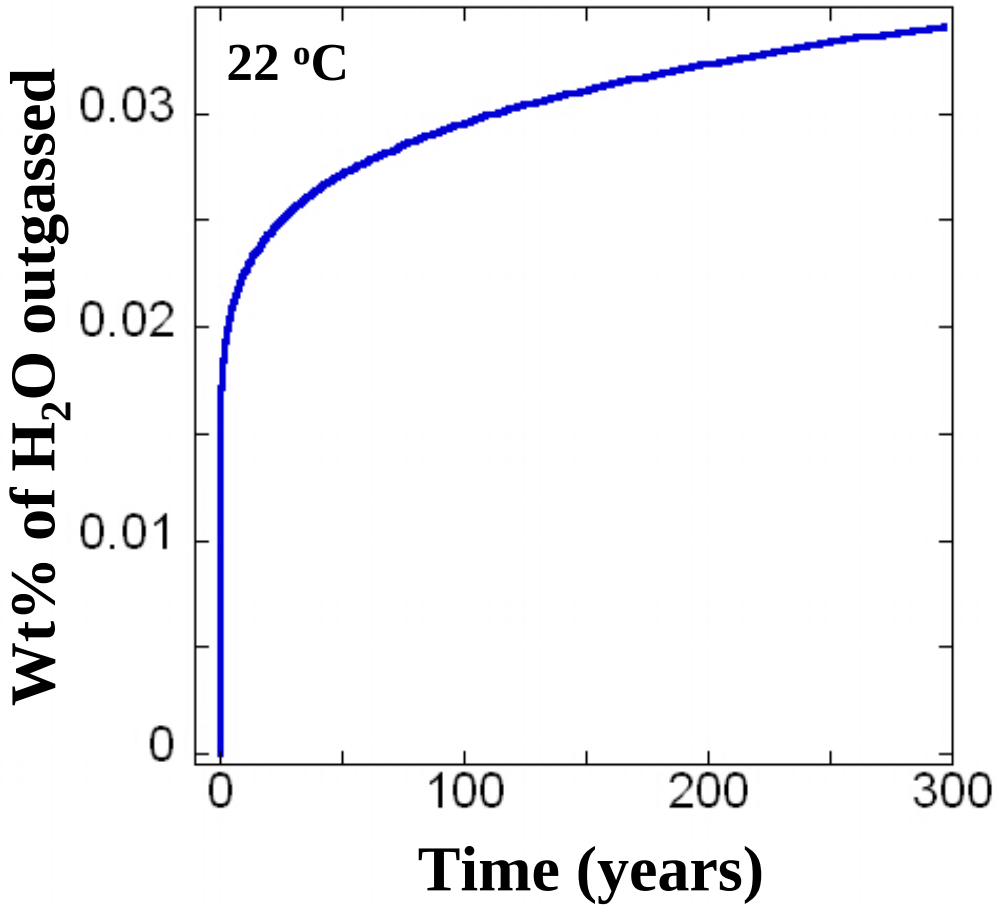
- The shapes of the kinetic prediction lines resemble that of the actual isothermal outgassing profiles.
- Within a 35 % error band around the Friedman prediction lines, there is a fair agreement between models and experiments.

Isothermal data

Isoconversion prediction

35% error band around Friedman

Prediction of moisture outgassing from TR55 at 22 ^{0}C



Only 0.03 wt% of H_2O out of a total of 0.23 wt% recorded by the TPD spectrum contributes to outgassing in a dry environment at room temperature

SUMMARY

- **The technique of isoconversional thermal analysis has been employed in the kinetic extraction and prediction of H_2O outgassing from TR55.**
- **The energy barriers for H_2O release from TR55 increase with increasing fractional H_2O release. At low temperatures, the H_2O outgassing process from TR55 can be interpreted as the release of H_2O from physisorbed water, then chemisorbed water with decreasing OH density from the surfaces of the silica filler.**
- **Model-independent predictions of H_2O outgassing based on the measured kinetics agree fairly well with actual isothermal outgassing. This agreement confirms the suitability of the isoconversional technique in the kinetic measurement and prediction of H_2O outgassing from silicones.**